

CLAIMS

1. Rubber reinforced vinyl aromatic (co)polymers having a strictly bimodal morphology, consisting of from 55 to 90% by weight of rigid polymeric matrix and from 10 to 45% by weight of a rubbery phase dispersed inside said rigid polymeric matrix, in the form of grafted and occluded particles and wherein said rubber particles consist of from 60 to 99% by weight of particles with a capsule or "core-shell" morphology and from 1 to 40% by weight of particles with a "salami" morphology, said percentages being measured on the basis of the weight of the rubber particles only.
2. The (co)polymers according to claim 1, wherein the core-shell particles have an average diameter ranging from 0.10 to 0.30  $\mu\text{m}$ , whereas the "salami"-structured particles have an average diameter ranging from 1 to 5  $\mu\text{m}$ .
3. The (co)polymers according to claim 1 or 2, wherein the elastomeric products capable of supplying a rubbery phase dispersed in the rigid polymeric matrix in the form of grafted and occluded particles with a capsule or "core-shell" morphology, are selected from homopolymers and copolymers of olefins or 1,3-alkadienes containing 40-100% by weight of 1,3-alkadiene monomer and 0-60% by weight of one or more mono-ethylenically

unsaturated monomers. --

4. The (co)polymers according to claim 3, wherein the elastomeric product is selected from linear di-block rubbers of the S-B type, wherein S represents a poly-  
5 styrene block having an average molecular weight Mw between 5,000 and 80,000, whereas B represents a poly-butadiene block with an average molecular weight Mw between 2,000 and 250,000.

5. The (co)polymers according to claim 3 or 4, wherein  
10 the amount of S block ranges from 10 to 50% by weight with respect to the total S-B rubber.

6. The (co)polymers according to claim 5, wherein the elastomeric product is a styrene-butadiene block co-  
15 polymer having a styrene content equal to 40% by weight and a viscosity in solution, measured at 23°C in a 5% by weight styrene solution, ranging from 35 to 50 cPs.

7. The (co)polymers according to claim 1 or 2, wherein the elastomeric products capable of providing a rub-  
20 bery phase dispersed in the rigid polymeric matrix in the form of grafted and occluded particles with a "salamini" morphology, are selected from homopolymers and copolymers of olefins or 1,3 alkadienes incompatible with the elastomeric products which provide the cap-  
25 sule rubbery phase.

8. The (co)polymers according to claim 7, wherein the criterion for selecting said incompatible elastomers is that the difference between the solubility parameter according to Hildebrand of the elastomer which produces the "capsule" rubbery particles and the solubility parameter according to Hildebrand of the elastomer which produces the "salami" rubbery particles, is higher than or equal to 0.5.

9. The (co)polymers according to claim 8, wherein the elastomeric product is polyisoprene with a viscosity in solution, measured at 23°C in a 5% by weight styrene solution, ranging from 100 to 1000 cPs.

10. A mass-continuous process for the preparation of rubber-reinforced vinyl aromatic (co)polymers with a strictly bimodal morphology, consisting of from 55 to 90% by weight of rigid polymeric matrix and from 10 to 45% by weight of a rubbery phase dispersed inside said rigid polymeric matrix, in the form of grafted and occluded particles and wherein said rubber particles consist of from 60 to 99% by weight of particles with a capsule or "core-shell" morphology and from 1 to 40% by weight of particles with a "salami" morphology, said process comprising:

i) dissolving from 3 to 20% by weight of a rubber selected from homopolymers and copolymers of 1,3-

alkadienes containing 40-100% by weight of 1,3-alkadiene monomer and 0-60% by weight of one or more mono-ethylenically unsaturated monomers, having a solubility parameter ( $\delta_1$ ), and from 0.05 to 8.0% by weight of a rubber selected from homopolymers and copolymers of olefins or 1,3-alkadienes incompatible with the previous rubber, having a solubility parameter ( $\delta_2$ ) which is such that  $\delta_1 - \delta_2 \geq 0.5$ , in a liquid essentially consisting of at least one vinyl aromatic monomer;

ii) polymerizing the resulting solution at a temperature ranging from 50 to 250°C optionally in the presence of polymerization initiators and/or chain transfer agents;

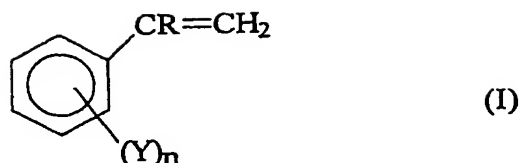
iii) recovering the vinyl aromatic (co)polymer thus obtained.

11. A mass-suspension process for the preparation of rubber-reinforced vinyl aromatic (co)polymers having a strictly bimodal morphology, consisting of from 55 to 90% by weight of a rigid polymeric matrix and from 10 to 45% by weight of a rubbery phase dispersed inside said rigid polymeric matrix in the form of grafted and occluded particles, and wherein said rubber particles consist of from 60 to 99% by weight of particles with a capsule or "core-shell" morphology and from 1 to 40%

by weight of particles with a "salami" morphology,  
said process including:

- 5 i) dissolving from 3 to 20% by weight of a rubber selected from homopolymers and copolymers of 1,3-alkadienes containing 40-100% by weight of 1,3-alkadiene monomer and 0-60% by weight of one or more mono-ethylenically unsaturated monomers, having the solubility parameter ( $\delta_1$ ), and from 0.05 to 8.0% by weight of a rubber selected from 10 homopolymers and copolymers of olefins or 1,3-alkadienes incompatible with the previous rubber, having the solubility parameter ( $\delta_2$ ), which is such that  $\delta_1 - \delta_2 \geq 0.5$ , in a liquid essentially consisting of at least one vinyl aromatic mono-mer; 15
- ii) pre-polymerizing the resulting solution at a temperature ranging from 50 to 250°C possibly in the presence of polymerization initiators and/or chain transfers, until phase inversion takes 20 place;
- iii) completing the polymerization in aqueous phase in the presence of suspending agents.

12. The process according to claim 10 or 11, wherein the vinyl aromatic monomer is selected from those having 25 general formula (I):



- 5        wherein R is a hydrogen or a methyl group, n is zero  
or an integer ranging from 1 to 5 and Y is a halogen  
such as chlorine or bromine, or an alkyl or alkoxy  
radical having from 1 to 4 carbon atoms.
13.    The process according to claim 10, 11 or 12, wherein  
10       rubbers are dissolved in the monomers, possibly in the  
presence of an inert solvent in quantities ranging  
from 5 to 20% by weight with respect to the total.
14.    The process according to any of the claims from 10 to  
15       13, wherein the dissolution of the rubbers in the  
monomer blend and possible solvent is carried out in a  
mixer maintained at a temperature not higher than  
100°C.
15.    The process according to any of the previous claims  
from 10 to 14, wherein, during the (pre)polymerization  
20       reaction in solution, the reactors are maintained at a  
pressure ranging from 0.5 to 5 bar and a temperature  
of between 70 and 150°C, whereas during the polymeri-  
zation reaction in suspension the temperature ranges  
from 100 to 170°C.
- 25    16.    The process according to any of the previous claims

from 10 to 15, wherein the initiators are added in quantities ranging from 0.005 to 0.5% by weight with respect to the monomer.

17. The process according to any of the previous claims  
5 from 10 to 16, wherein the chain transfer agents are added in quantities ranging from 0.005 to 0.5% by weight with respect to the monomer.

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